

ELECTRON CORRELATIONS IN THE HIGH T_c -COMPOUNDS

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Ab-initio correlation results for an idealized high T_c -compound are compared to density functional (DF) calculations for the same system. It is shown that and why the DF-charge distribution is wrong. The largest deficiency arises for the $Cu-d_{x^2-y^2}$ -occupation, arising from strong atomic correlations but mostly from anomalous neighbor Cu -spin correlations. Both features are beyond the range of the homogeneous electron gas approximation underlying the DF-schemes. The ab-initio results also exclude a description of the real system in a Mott-Hubbard scenario, that is mostly chosen in theory. Conditions for models are derived that are able to describe the high- T_c -compounds.

1. INTRODUCTION

In the past, two approaches have dominated the attempts to understand the electronic structure of the high- T_C compounds. The first is by ab-initio DF-calculations within the local density approximation (LDA), and the second is by very particular models.

The LDA calculations suffer from the underlying homogeneous electron gas approximation for exchange and correlations. They are able to represent properties like equilibrium lattice constants, phonons, or the Fermi surface, but are unable to reproduce the magnetic phase at half filling, and have deficiencies for the band masses. The obtained electron lattice coupling is too small for the explanation of superconductivity.

The particular models are mostly restricted to the $Cu-O$ -planes. The description of the electrons in these planes is usually further restricted to a single band Hubbard model in the strong correlation limit or to a t-J model. Such a model can explain the magnetism of the so called half-filled planes, and deliberate Fermi surfaces can be generated by particular parametrizations. A connection to the microscopic reality however, or even the unequivocal construction of a plausible new mechanism of superconductivity, could not yet be obtained.

We had been able to pursue a different approach that neither suffers from the uncontrollable shortcomings of the LDA, nor from an equally uncontrollable ad hoc choice of a particular model. With the help of the Local Ansatz (LA), we were able to perform an ab-initio correlation calculation for an idealized high- T_c compound¹.

It is generally agreed that a basic understanding for the high T_c -compounds can be gained from the treatment of a simplified idealized compound, namely a single charged $Cu-O$ -plane. Actually most models make use of this approximation. Our calculation was restricted to such a system, or rather to its so called infinite layer generalization into three dimensions.

In the following, we will compare the LA-results to similar LDA-calculations, and will unequivocally determine the deficiencies of the LDA, and their causes. We will also depict a few important correlation results and give a critical valuation of the most often used models.

2. COMPUTATION METHOD

The LA allows the ab-initio computation of the correlated ground state of a solid. Starting point for the correlation treatment is a self consistent field (SCF) or Hartree-Fock calculation for this solid, resulting in the uncorrelated single-particle ground state Ψ_{SCF} . This SCF-calculation was performed by the program Crystal². The latter program uses atom centered Gauss type orbitals (GTO) as a basis, as does the LA.

Within the LA, the following variational ansatz is made for the correlated ground state:

$$|\Psi_{\text{corr}}\rangle = e^{-S}|\Psi_{\text{SCF}}\rangle \quad (1)$$

$$S = \sum_{\nu} \eta_{\nu} O_{\nu} \quad (2)$$

$$O_{\nu} = \begin{cases} n_{i\uparrow}n_{i\downarrow} \\ n_i n_j \\ \vec{s}_i \cdot \vec{s}_j \\ \{n_{i\uparrow}(a_{i\downarrow}^{\dagger}a_{j\downarrow} - a_{j\downarrow}^{\dagger}a_{i\downarrow})\} + \{\uparrow \leftrightarrow \downarrow\} \\ n_i \end{cases} . \quad (3)$$

The η 's serve as variational parameters. The $n_{i\sigma}$ and \vec{s}_i are density and spin operators for an electron in the local state $a_{i\uparrow}^{\dagger}$, represented by the orbital

$$g_i(\vec{r}) = \sum_j \gamma_{ij} f_j(\vec{r}) \quad (4)$$

where the $f_i(\vec{r})$ are the (GTO like) basis orbitals. The operators have an obvious meaning. The first operator $n_{i\uparrow}n_{i\downarrow}$, for example, when applied to $|\Psi_{\text{SCF}}\rangle$, projects out all configurations with two electrons in orbital $g_i(\vec{r})$. In connection with the variational parameter η_{ν} , it partially suppresses those configurations. Similarly, the operators $n_i n_j$ describe density corre-

lations between electrons in local orbitals $g_i(\vec{r})$ and $g_j(\vec{r})$. The operators $\vec{s}_i \cdot \vec{s}_j$ generate spin correlations. The fourth kind of operators is of the form of $[O_\nu, H_0]_-$, where H_0 represents the single-particle Hamiltonian. These operators refine the ansatz with respect to the band energy of the electrons involved. The original operators of eq. 3 are next modified by subtracting the contracted contributions in each of them. The corrected operators when applied to $|\Psi_{\text{SCF}}\rangle$ contain only two-particle excitations, and the corrected last kind of operators in eq. 3 covers local single particle excitations, i.e. it allows for changes in occupations.

The variational parameters η_ν are chosen to optimize the energy

$$E_G = \frac{\langle \Psi_{\text{corr}} | H | \Psi_{\text{corr}} \rangle}{\langle \Psi_{\text{corr}} | \Psi_{\text{corr}} \rangle} \quad (5)$$

$$= \langle \Psi_{\text{corr}} | H | \Psi_{\text{corr}} \rangle_c \quad (6)$$

In the last equation, the subscript c indicates that only connected diagram contributions are summed up. This expression cannot be evaluated exactly. The standard approximation is an expansion in powers of η , up to second order,

$$E_G = E_{\text{SCF}} + E_{\text{corr}} \quad (7)$$

$$E_{\text{corr}} = - \sum_{\nu} \eta_{\nu} \langle O_{\nu}^{\dagger} H \rangle \quad (8)$$

$$0 = - \sum_{\nu} \eta_{\nu} \langle O_{\nu}^{\dagger} H \rangle + \sum_{\nu, \mu} \eta_{\nu} \eta_{\mu} \langle O_{\nu}^{\dagger} H O_{\mu} \rangle_c \quad (9)$$

Here, $\langle A \rangle$ means the expectation value of the operator A within $|\Psi_{\text{SCF}}\rangle$. This is a weak correlation approximation that blows up when correlations turn too strong. For the high- T_c 's no such problems arose, indicating that the Mott-Hubbard limit does not apply.

The local orbitals in eq. 4 are connected to a single atom only and are built from its basis orbitals. Standard Quantum Chemistry (QC) methods also start from a SCF-calculation and add correlations with the help of one-and two-particle operators. However, the QC-operators are constructed from orthogonal sets of occupied and/or unoccupied orbitals, a construction that fails for metals. The restriction to local orbitals and the particular construction of correlation operators from these local orbitals is the essential approximation of the LA in comparison to QC. It allows even to treat metals with QC accuracy.

For the high- T_c application, only operators built from atomic orbitals were used. The atomic orbitals are unequivocally determined from the SCF-ground state by the condition that they are built from basis orbitals on the respective atoms only and that they cover a maximal

fraction of the full occupied space. The resulting orbitals are next Löwdin-orthogonalized to each other. More localized subatomic orbitals were not used in this application.

The calculated system is formally be described as $SrCuO_2$. It is half-filled and has an antiferromagnetic ground state. However, in all calculations, not this antiferromagnetic ground state but a metastable non magnetic state was treated since we are not interested in the magnetic order but in the electronic properties of the doped high- T_c compounds. This approach is necessary because the Crystal program requires unit cells with integer filling, but we wanted to avoid large unit cells. We took care that none of the computed results was influenced by the proximity to the magnetic instability.

Being interested on in-plane features, we choose a good basis for the in plane Cu - and O - atoms, but added no valence basis orbitals for the Sr -atoms. This leads to a charging of the planes with 2 electrons per Cu -atom, and renders the interplane coupling negligible. For more details of the basis choice, of the structure of the idealized system, and of the correlation calculations, we refer to ref. 1).

3. ATOMIC CHARGE DISTRIBUTION

Being unequivocally defined, the atomic orbitals, generated for correlation purposes, are also a perfect basis for a detailed charge analysis. This representation avoids all non orthogonality problems of a standard Mulliken population analysis.

The partial charge distributions $n_i(\Psi) = \langle \Psi | \sum_{\sigma} n_{i\sigma} | \Psi \rangle$ are presented in table 1 for different states Ψ . The first row contains the values for $\Psi = \Psi_{SCF}$. The sum over the partial occupations approaches the number of valence electrons within 0.02. This proximity rectifies the condensation into atomic orbitals and the specific method of their computation.

With the addition of correlations, a relatively large charge transfer occurs. Ultimately, it is a charge transfer mostly from the $Cu3d_{x^2-y^2}$ -orbitals into the $O2p$ -orbitals. However, for its understanding it is necessary to progress stepwise. A first step is the addition of atomic correlations which lead to a large correlation energy gain. The dominant charge transfer due to the atomic correlations is from the $Cu3d_{x^2-y^2}$ -orbitals to the $Cu4s, 4p$ -orbitals, followed by a secondary redistribution from the $Cu4s, 4p$ -orbitals to the $O2p$ -orbitals. Over all, 0.18 electrons are removed from the $Cu3d_{x^2-y^2}$ -orbitals, and put into the $Cu4s, p$ -shell (0.13) and the $O2s, p$ -shells (2×0.03). More than 80 percent of this charge transfer arise from the inclusion of the operators $n_{i\uparrow}n_{i\downarrow}$ for the $Cu3d_{x^2-y^2}$ -orbitals, the remaining part stems from the same operators for the $4s, p$ -orbitals. For an explanation, we refer to ref 1).

Orbital	HF	on site corr	nn corr	full corr	LDA
$Cu3d_{x^2-y^2}$	1.51	1.33	1.17	1.15	1.53
$Cu3d_{z^2}$	1.95	1.94	1.94	1.94	1.90
$Cu3d_{xy}, 3d_{xz}, 3d_{yz}$	2.00	2.00	2.00	2.00	1.99
$Cu4s$	0.50	0.55	0.57	0.58	0.64
$Cu4p_{pl}$	0.30	0.33	0.34	0.34	0.31
$Cu4p_{\perp}$	0.09	0.11	0.11	0.11	0.18
$O2s$	1.82	1.82	1.81	1.81	1.80
$O2p_b$	1.42	1.48	1.57	1.58	1.39
$O2p_{orth}$	1.97	1.96	1.96	1.96	1.94
$O2p_{\perp}$	1.95	1.93	1.92	1.91	1.92

Table 1: Charge distributions for the SCF ground state and with correlations added, in comparison to LDA results. The subindices of the p -orbitals have the following meaning: \perp perpendicular to plane, pl in plane, b in bond direction, $orth$ in plane perp. to bond

When neighbor correlations are included, then an additional charge transfer of the same magnitude as the one due to on-site correlations occurs. It is dominantly from the $Cu3d_{x^2-y^2}$ -orbitals to the $O2p_b$ -orbitals, and is due to a particular spin correlation between neighbor Cu -sites that will be discussed later. The longer range contributions that were covered by the present computations lead to a further but small transfer of the same kind. For an error analysis, we refer to ref. 1) again.

The latest version of the program Crystal² also allows to perform LDA-calculations within the same basis set as used for the SCF-calculation. The resulting LDA charge distribution is analysed in the same way as done before for the SCF-case. Most alternative LDA-schemes have no atom centered basis. Thus, their ground state results can not be fully decomposed into atomic occupations. Only partial results were so far available, mostly from tight binding fits to the energy bands. Here, the first full LDA charge analysis is given.

The LDA-result is included in table 1. The occupations of the $3d$ -orbitals are in very good agreement with earlier LDA results (for citations, see Ref 1)). There is a close agreement with the SCF-result. Only orbitals almost filled in LDA are even more filled in SCF-approximation, resulting from the well known band spreading of the SCF. Correlations partially undo this. The proximity to SCF indicates that none of the correlation corrections are contained in the LDA result. It is plausible that the anomalous neighbor correlation effects can not be covered by the homogeneous electron gas approximation, but it was somewhat astonishing that the atomic correlation effects are also completely disregarded in LDA.

These occupation results demonstrate why LDA must be very deficient for the high T_c -

compounds. A consequence for the band structure can be easily derived. When keeping the LDA hopping terms in the single-particle Hamiltonian but shifting the crystal field terms so that the resulting single-particle ground state has the correct charge distribution, then the Fermi surface stays the same, but the conduction band shrinks by half, bringing it into much closer agreement to experiment. More details will be given elsewhere³.

4. SPIN CORRELATIONS AWAY FROM HALF FILLING

All LA results discussed so far were connected to LDA results. But in contrast to the LDA, the LA obtains also full information for the correlated ground state, and in particular correlation functions. In the following, we will deal with the surprising anomalous neighbor *Cu*-spin correlations. These are connected to a charge transfer from the two *Cu*-atoms into the inbetween *O*-atom because the latter enhances the antiferromagnetic coupling and further reduces the charge fluctuations on all three involved atoms. This is a correlation feature of the delocalized electron system. It is not at all connected to a Mott-Hubbard transition which can be ruled out by our results. These spin correlations mutually enhance each other. Even without any long range magnetic order in the metastable metallic state, they are so big that the repulsive effect of the on-site *Cu*-correlation hole is overcompensated, and that electrons with differing spins have a higher probability to be close to each other (i.e. up to neighbor sites) than without correlations.

This finding has a similarity to the so called renormalized valence bond (RVB) picture that had been proposed as a mechanism for superconductivity⁴, and that also leads to a strong neighbor spin correlation. While the RVB approach is only valid close to the Mott-Hubbard transition, our results arise already for weak correlations and are also present at large dopings.

These short range magnetic correlation features are next compared to experiment. This can only be done outside the magnetically ordered phase. While the ab-initio calculations themselves can not be extended to fractional charging due to the Crystal program limitations, a valuable alternative is to condense the half-filled case informations to a model, and to extend this model to differing fillings. Such a model needs to describe the conduction band well, and also needs to explicitly include the electronic interactions. We had chosen the smallest possible model that contains the *Cu*- $3d_{x^2-y^2}$ orbitals, the *O*- $2p_b$ orbitals, and also the *Cu*- $4s$ orbitals. The latter orbitals were needed to obtain a correct occupation of the other two orbitals, necessary for the short range spin correlations. A three band model (without the $4s$ -orbitals) turned out to be very deficient. Even our model choice caused shortcomings because we had

to move charge from the 4s-orbitals into the 2p-orbitals in order to preserve the correct Fermi surface. This might be overcome in the future by extending the model by 4p-orbitals.

The hopping terms for this model were taken from an LDA-band structure fit found in the literature⁵, and the crystal field terms were obtained from the required occupations. As interaction, Hubbard interaction terms U_i were included for the individual orbitals. Their value was set so that the atomic correlation functions obtained by the LA for the model were the same as the ab-initio results¹. This model describes the atomic correlations correctly but gives, probably for the deviations in the occupations, too small neighbor spin correlations. We therefore performed a parallel calculation with a U_{3d} that was enhanced by 20 percent.

With this model we calculated the spin correlation function

$$S(\vec{Q}) = \sum_{i,j,\vec{G}} \langle \Psi_{corr} | \vec{s}_i(0) \vec{s}_j(\vec{G}) | \Psi_{corr} \rangle e^{i\vec{Q}(\vec{r}_i - \vec{r}_j - \vec{G})} \quad . \quad (10)$$

of the model with 15 percent doping. Here, i, j runs over the atomic orbitals on sites r_i, r_j in the unit cell, and G describes the lattice summation. This function can be compared to the corresponding, experimentally measured spin correlation function⁷ $S(\vec{Q})$ for the metallic compound $La_{0.85}Sr_{0.15}Cu_2O_4$. The latter is no equal time correlation function but only energy integrated up to 0.15eV.

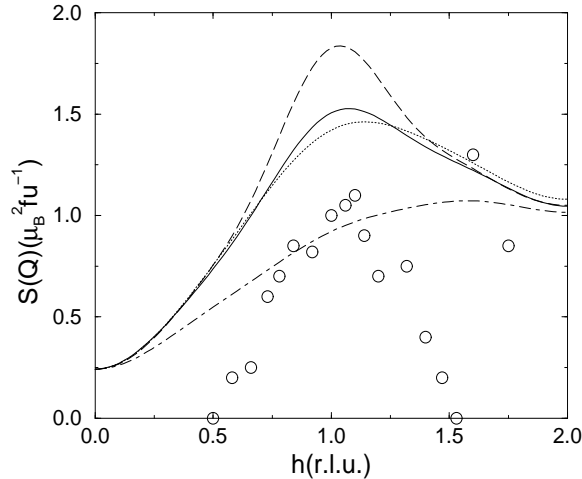


Figure 1: Equal time spin correlation function $S(Q)$ for $\vec{Q} = (h, h, 0)$ in comparison to experiment⁶ (empty circles). Given are the results of the HF-ground state (broken-dotted curve), the 5 atom cluster result (dotted line) and the 9 atom cluster result (continuous line) for $U_{3d}=6.3\text{eV}$, and the 9 atom cluster result for $U_{3d}=7.8\text{eV}$.

Fig. 1 contains the experimental and theoretical results for the diagonal (1,1) axis. The

zone boundary is at $h=1$, the intensity is given per formula unit which here is equivalent to a unit cell or to a single *Cu* atom.

The lowest curve represents the result for the single-particle ground state. It represents the exchange holes. As the finite value at $h = 0$ indicates, the summation in eq. 10 was not brought to convergency. The maximal deviation occurs for $h = 0$ where the contributions from all missing terms add up. Due to dephasing, the correction is very much smaller for finite h .

Next, short range correlations as they are deduced from a single coherent 5 *Cu* cluster calculation are included (dotted curve). Here, the nearest neighbor *Cu*–*Cu* correlations come into play and cause a peak at the zone boundary ($h = 1$). When extending the correlation treatment to a 9 *Cu* cluster, the peak narrows somewhat and enhances a little (continuous curve). Finally, also the corresponding values with enlarged U (7.8eV instead of 6.3eV) are given (broken curve).

As expected, the theoretical equal time correlation function is always larger than the experimental correlation function whose energy integration extends only to 0.15 eV. One would expect that a sizable part of the correlation function, namely the one already obtained by Ψ_{SCF} can definitely not be seen by the slow neutrons. Consequently, all remaining contributions need to be seen in the experiment. This might occur because the electrons partially localize due to a charge density wave formation in the case of the treated compound.

It should be noted that neither Hubbard model nor t-J-model results are able to explain such a strong inelastic magnetic scattering at 15 percent doping. Also a 3 band model would definitively fail if reasonable Hubbard interaction terms were chosen. Even the 4 band model used here displays deficiencies.

Our results indicate that the origin of the inelastic magnetic scattering might well be completely disconnected from the magnetic order at half filling, and might be explained by the anomalous short range correlations found over a large range of doping. At least the theoretical Q-dependence matches the experiment very well.

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